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(54) Title: PROCESS FOR THE PREPARATION OF TITANIUM COMPLEXES

(57) Abstract: A new process is disclosed, particularly simple, convenient and practical, for the direct synthesis of titanium complexes of the formula (I): $(D)(ZR^1_m)_n(A)TiL_pX_q$, wherein $(ZR^1_m)_n$ is a divalent group bridging D and A; D is a delocalized π -bonded moiety, which is bound in an η^5 bonding mode to Ti, and is preferably a Cp moiety; A is -O-, -S-, -N(R²)- or -P(R²)-, wherein R² is hydrogen, alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl; L are monoanionic sigma ligands selected from alkyl, cycloalkyl, aryl, alkylaryl and arylalkyl groups; m is 1 or 2; n is 1-3; p is 1 or 2, q is 0 or 1 and p + q = 2; said process comprises reacting a ligand of formula (H-D)(ZR¹_m)_n(A-H) with about 1 molar equivalent of TiX₄ in the presence of about (2 + p) molar equivalent of L_jB or LMgX, wherein X is halogen or -OR', B is an alkaline or alkaline-earth metal, and j is 1 or 2.

PROCESS FOR THE PREPARATION OF TITANIUM COMPLEXES

FIELD OF THE INVENTION

The present invention relates to a new process, particularly simple, convenient and practical, for the preparation of complexes of titanium, preferably monocyclopentadienyl titanium dihydrocarbyl complexes; more specifically, it relates to a process for the direct synthesis of complexes wherein the titanium atom is linked to two sigma ligands selected from the group consisting of linear or branched, saturated or unsaturated C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl and C₇-C₂₀ arylalkyl radicals, optionally containing Si or Ge atoms.

These complexes are useful as catalyst components in the polymerization of olefins, in association with suitable activating cocatalysts.

PRIOR ART DISCLOSURE

Homogeneous catalytic systems based on constrained geometry catalysts in association with useful cocatalysts are well known in the state of the art and are widely used in the polymerization reaction of olefins, as described for instance in EP-A-416,815, EP-A-420,436, EP-A-671,404, EP-A-643,066 and WO 91/04257.

These homogeneous catalytic systems are based on mono-cyclopentadienyl metal dihalide coordination complexes, wherein the sigma ligands of the central metal atom are halogen, and usually chlorine.

In known prior art processes, the synthesis of the metal dihalide complexes is often troublesome and much lower than quantitative. Said complexes may be produced by contacting the metal reactant (usually MX₄) and a group I metal salt (usually the dilithium salt) or a Grignard salt of the cyclopentadienyl compound; while this reaction may be favorably carried out to produce zirconium dihalide complexes, it shows only very poor yields in the production of titanium dihalide complexes, due to the reduction of Ti(IV) to Ti(III).

For instance, M. Waymouth et al. (*Organometallics* 16:2879-2885, 1997) prepared indenyl-amido titanium dichloride complexes by treating the dilithium salt of (tert-butylamido)(dimethyl)(indenyl)silane (obtained by reacting the ligand with 2BuLi) with TiCl₄(THF)₂; the yields for this synthesis were quite low (< 20%).

Besides the very low final yields, said reactions have the disadvantage of requiring very low temperatures (-78°C). In fact, the dianion of the monocyclopentadienyl ligand compound

requires a multi-step, laborious recovery and purification procedure, before being reacted with an halogenating agent.

Another disadvantage resides in the fact that, since the reaction has to be carried out in aprotic polar solvents, in order to facilitate the handling of the metal tetrahalide reactant which is air and moisture sensitive, prior to the reaction step the transition metal tetrahalide compound is typically converted to its ether-adduct in a separate step with THF or diethyl ether. This adduct formation step in itself proceeds with difficulty, requiring low to very low temperatures, and an inert atmosphere. The adduct is usually recovered before it is reacted with the dianionic derivative of the ligand. The yield of the adduct formation steps is less than quantitative.

Furthermore, the reaction mixture of the transition metal tetrahalide compound and the dianion of the bridged cyclopentadienyl ligand compound requires a multi-step, laborious recovery and purification procedure. Typically, after the reaction step, the solvent is removed, the product re-dissolved by adding dichloromethane or toluene or a mixture thereof, the metal halide byproduct (typically lithium chloride) removed by filtration of the mixture, the solvent removed at least partially, followed by re-dissolving the solid product and crystallizing the product, optionally followed by one or more further recrystallization procedures.

In a preferred process known in the state of the art, the dianionic salt of the monocyclopentadienyl ligand is reacted with a metal compound wherein the metal is in a lower oxidation state than in the desired final complex, for instance Ti(III) compounds; thereafter, the resulting complex has to be contacted with an oxidizing agent (such as AgCl or PbCl₂), in order to raise the oxidation state of the metal to form the desired titanium (IV) dihalide complex.

Apart from requiring an extra reaction step (i.e. the oxidation step), the intermediate monohalide coordination complex of Ti(III) is thermally unstable; therefore, reaction yields are usually unsatisfactory.

For instance, in *Organometallics* 16:2879-2885, 1997 is described the preparation of a bridged mono(substituted cyclopentadienyl) titanium dichloride complex by treating the THF-adduct of TiCl₃ with the dimagnesium salt of [(R-amide)dimethylsilyl](tert-butyl)cyclopentadienide (obtained by deprotonation of the ligand with *i*PrMgCl), followed by PbCl₂ oxidation; the yields were only of 52% in case of R = *t*Bu and 16% in case of R = CHMePh. Moreover, in the case of indenyl-amido titanium complexes, reaction of the indenyl dimagnesium dichloride salts with TiCl₃(THF)₃ followed by PbCl₂ oxidation was completely unsuccessful.

The corresponding dihydrocarbon derivatives, particularly dimethyl ones, have been developed and are widely used as catalyst components for olefin polymerization reactions, in association with suitable cocatalysts, such as alumoxanes and borate salts, e.g. $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ or $[\text{HN}(\text{n-Bu})_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$.

When the sigma ligands of the central metal atom are alkyl or aryl groups, the above metal complexes may not be expediently synthesized by the existing methodology; in fact, prior art processes imply always the synthesis of the metal complex dihalide, that is subsequently hydrocarbylated by ligand exchange with an appropriate hydrocarbylating agent to the target product, thus leading to unsatisfactory total yields and requiring at least the following two process steps:

- (1) preparing the halide metal coordination complex, usually the dichloride, by reacting a suitable ligand with MX_4 , wherein X is halogen (usually $\text{TiCl}_4(\text{THF})_2$ or ZrCl_4); or alternatively preparing the halide metal coordination complex by reacting a suitable ligand with MX_3 (usually $\text{TiCl}_3(\text{THF})_3$) and thereafter contacting the product with an oxidizing agent (usually AgCl or PbCl_2);
- (2) converting the dihalide complex obtained in step (1) into the corresponding dialkyl complex, by substitution of the halogens linked to the metal atom with the desired alkyl or aryl groups, by means of an alkylating agent such as alkyllithium, dialkylmagnesium or the corresponding Grignard reagent.

As already evidenced above, process step (1), leading to the metal monohalide complex, is often troublesome (requiring very low reaction temperatures) and not quantitative; in particular, very poor yields are obtained when TiCl_4 or its adducts are used as reactants, due to the abundant reduction of the metal. On the opposite, in case that Ti(III) derivatives are used as the reactants, more acceptable yields are obtained, but the resulting dihalide complex has to be contacted with an oxidizing agent, in order to raise the oxidation state of the metal to form the desired dihalide complex. Therefore, these preparation processes inherently have the disadvantages associated with the preparations of the metal dihalide complexes.

Finally, in order to achieve the desired dialkyl metal complex, the metal dichloride complex has to be treated with an alkylating agent, such as MeLi (step (2)); therefore, a further reaction step is required thus lowering notably the total reaction yields and rendering the whole process

more laborious and time consuming.

According to the literature procedures (Jun Okuda et al., *Journal of Organometallic Chemistry*, 520:245-248, 1996), dimethylsilandiyl(tert-butylamido)(indenyl) titanium dimethyl can be obtained at best in two reaction steps, in an unsatisfactory total yield. More specifically, in the cited reference, Okuda obtained the above Ti(IV) dichloride complex by the reaction of the dilithium derivative $\text{Li}_2[\text{Ind-SiMe}_2\text{-NCMe}_3]$ (obtained in a yield of 90% by reacting the ligand and BuLi, at low temperature) with a suspension of $\text{TiCl}_3(\text{THF})_3$ in THF, followed by oxidation using PbCl_2 of the obtained titanium (III), in a yield of 94%. The Ti(IV) dichloride complex was then alkylated at -78°C by reacting the dihalide metal complex with methylmagnesium chloride, thus obtaining the dimethyl complex $\text{Ti}[\text{Ind-SiMe}_2\text{-NCMe}_3]\text{Me}_2$ in 49% yield; therefore, starting from the ligand, the resulting total yield is not satisfactory ($90 \cdot 94 \cdot 49 / 10,000 = 41.5\%$).

J. Marks et al. (*Organometallics*, 16:3649-3657, 1997) obtained the synthesis of dimethylsilandiyl(tert-butylamido)(η^5 -tetramethyl-cyclopentadienyl) titanium dimethyl in an unsatisfactory total yield of 31.7%, with the following steps: 1) reaction the ligand of (tert-butylamido)(dimethyl)(η^5 -tetramethyl-cyclopentadienyl)silane with 2BuLi in Et_2O at -78°C , to give the ligand dilithium salt in 90% yield; 2) reacting the obtained dilithium salt with the appropriate metal halide ($\text{TiCl}_3(\text{THF})_3$) at very low temperature (-78°C), followed by oxidation with PbCl_2 or AgCl , with a yield of 63%; 3) final alkylation of the obtained metal dichloride with MeLi, at very low temperature (-78°C), with a yield of 56%. Therefore, the above synthesis provides the desired titanium dialkyl complex in an overall yield lower than 32%, with three cooling cycles.

In regard to alternative synthetic strategies for the production of titanium monocyclopentadienyl-amido complexes, the $\text{Ti}(\text{NR}_2)_4$ precursor amine elimination approach has provided in general a more efficient preparation than conventional salt elimination synthetic routes (see W.A. Herrmann et al., *Journal of Organometallic Chemistry*, 482:169-181, 1994).

However, in the above cited reference (*Organometallics*, 16:3649-3657, 1997), this route is reported to be unsuitable for titanium diamido complexes (ligand) $\text{Ti}(\text{NMe}_2)_2$ and leads instead to a myriad of undesired products (while for Zr complexes, only a single product is afforded).

Furthermore, although the amine elimination route provides an efficient preparation of Cp-unsubstituted $\text{Me}_2\text{Si}(\text{C}_3\text{H}_4)(t\text{BuN})\text{M}(\text{NMe}_2)_2$ ($\text{M} = \text{Ti}$ or Zr) analogues, the amido complexes cannot be protonically converted to the corresponding dichloride derivatives without the formation of dimethylamine adducts.

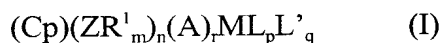
For subsequent catalysis, it is critical that the amido complexes be converted to dichloride or ideally to dialkyl polymerization catalyst precursors, because amido-derived catalysts are significantly less active than chloride or alkyl-derived catalysts.

An alternative synthetic route is reported in the international patent application WO 95/19984, which describes a process for preparing bridged mono- and bis(cyclopentadienyl) metal dihydrocarbyloxy coordination complexes by contacting, in the presence of an aprotic organic diluent, a metal compound of formula $\text{M}(\text{OR})_4$ with the dianionic salt of the corresponding ligand; by treatment of said metal dihydrocarbyloxy coordination complexes with a hydrocarbylation agent or an halogenation agent, the corresponding metal dihydrocarbyl or dihalide coordination complexes may be obtained.

Also in this case, in order to achieve the desired dialkyl metal complex, it is necessary to pass through the metal dihydrocarbyloxy derivative; although this process avoids the disadvantages associated with the preparations of the metal dihalide complexes, it requires a further reaction step, thus lowering the total reaction yields and rendering the whole process more laborious and time consuming.

Therefore, the prior art processes for producing constrained geometry catalysts, and in general metal complexes having hydrocarbon sigma ligands bonded to the central metal atom, are inadequate for a commercially viable and practical production of said derivatives, for use as catalyst components in olefin polymerization; it is felt the need for a simpler and more convenient and practical method to produce the above metal derivatives in satisfactory yields.

The international patent application WO 99/36427 (appl. no. PCT/EP 99/00188), in the name of the same Applicant, describes a process for the preparation of metallocene compounds of formula (I):



wherein $(\text{ZR}^1_{\text{m}})_n$ is a divalent group bridging Cp and A, Z being C, Si, Ge, N or P, and the R^1 groups being hydrogen or hydrocarbon groups;

Cp is a cyclopentadienyl group;

A is a cyclopentadienyl group or may be -O-, -S- or -N(R²)-, wherein R² is hydrogen or an hydrocarbon group;

M is a transition metal of groups 3-6 or of the lanthanide or actinide groups;

the substituents L are monoanionic hydrocarbon sigma ligands;

the substituents L' are halogens or -OR, wherein R is hydrogen or an hydrocarbon group;

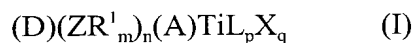
m is 1 or 2; **n** is 0-4; **r** is 0 or 1; **p** is 1-3; and **q** is 0-2.

The process comprises reacting a ligand of formula (Y-Cp)(ZR¹_m)_n(A-Y)_r with at least (1+r+p) molar equivalents of a compound of formula L_jB or LMgL', wherein Cp, A, Z, R¹, **m**, **n**, **p**, **r**, L and L' have the meaning reported above; the groups Y, the same or different from each other, are suitable leaving groups; B is an alkaline or alkaline-earth metal; and **j** is 1 or 2, **j** being equal to 1 when B is an alkaline metal, and **j** being equal to 2 when B is an alkaline-earth metal; and reacting the product obtained from step (1) with at least 1 molar equivalent of a compound of formula ML'_s, wherein M and L' have the meaning reported above; **s** is an integer corresponding to the oxidation state of the metal and ranges from 3 to 6.

The described process is used in the preparation of metallocenes of Ti, Zr or Hf, preferably of bis-cyclopentadienyl metallocenes of Zr. All the examples refer to the preparation of dialkyl derivatives of Zr.

SUMMARY OF THE INVENTION

The Applicant has now unexpectedly found a new process for the preparation of titanium complexes having hydrocarbon sigma ligands bonded to the central metal atom; more specifically, it is an object of the present invention a direct one-pot synthesis of titanium complexes having formula (I):



wherein:

(ZR¹_m)_n is a divalent group bridging D and A, Z being C, Si, Ge, N, P or B, and the R¹ groups, equal or different from each other, being hydrogen or linear or branched, saturated or unsaturated C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl or C₇-C₂₀ arylalkyl groups; or two R¹ may form together a ring; **m** is 1 or 2; **n** is an integer ranging from 1 to 3;

D is a delocalized π-bonded moiety, which is bound in a η⁵ bonding mode to Ti, and preferably is a substituted or unsubstituted cyclopentadienyl moiety (herein referred to as Cp);

A is a divalent anionic group selected from -O-, -S-, -N(R²)- or -P(R²)-, wherein R² is

hydrogen, a linear or branched, saturated or unsaturated C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl or C₇-C₂₀ arylalkyl, optionally containing -OR', -SR', -NR'₂ or -PR'₂ groups, wherein R' is a C₁-C₁₀ alkyl group;

Ti is titanium;

the substituents L, same or different from each other, are monoanionic sigma ligands selected from the group consisting of linear or branched, saturated or unsaturated C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl and C₇-C₂₀ arylalkyl groups, optionally containing one or more Si or Ge atoms; preferably, the substituents L are the same;

X is halogen or -OR', wherein R' is a C₁-C₁₀ alkyl group;

p is 1 or 2, preferably 2; **q** is 0 or 1, and **p + q = 2**

said process being characterized by comprising the following steps:

- (1) reacting a ligand of formula (H-D)(ZR'_m)_n(A-H) with about (2 + **p**) molar equivalents of a compound of formula L_jB or LMgX, wherein D, A, Z, R', **m**, **n**, **p**, L and X have the meaning reported above; B is an alkaline or alkaline-earth metal; **j** is 1 or 2, **j** being equal to 1 when B is an alkaline metal, and **j** being equal to 2 when B is an alkaline-earth metal; and
- (2) reacting the product obtained from step (1) with about 1 molar equivalent of a compound of formula TiX₄, wherein X has the meaning reported above.

DETAILED DESCRIPTION OF THE INVENTION

The process of the invention allows to obtain titanium complexes wherein the metal atom bears one or two sigma-bonded hydrocarbon substituents, in a simple, rapid and economic way, leading to the desired products with a one-step process starting from the suitable ligands; furthermore, said process leads to final yields much higher than the ones obtainable with the procedures known in the state of the art, therefore allowing a convenient industrial exploitation of the above metallocene compounds as catalyst components in the polymerization of olefins.

The very good yields obtainable with the process according to the present invention are totally unexpected in the light of the results obtained in the prior art literature by contacting a titanium reactant (such as TiX₄) and the dilithium salt of the cyclopentadienyl ligand; as already evidenced above, in that case, only poor yields were obtained in the production of titanium dihalide complexes, due to the partial reduction of Ti(IV) to Ti(III).

On the opposite, in the process of the invention the reduction of Ti(IV) is unexpectedly negligible, thus leading to the desired complex in high yields.

In the titanium complexes of formula (I), the divalent bridge $(ZR^1_m)_n$ is preferably selected from the group consisting of CR^1_2 , $(CR^1_2)_2$, $(CR^1_2)_3$, $CR^1=CR^1$, SiR^1_2 , $(SiR^1_2)_2$, $CR^1_2-SiR^1_2$, GeR^1_2 , NR^1 , PR^1 and BR^1 , R^1 having the meaning reported above; more preferably, said divalent bridge is $Si(CH_3)_2$, $SiPh_2$, CH_2 , $(CH_2)_2$, $(CH_2)_3$ or $C(CH_3)_2$.

The variable **m** is 1 or 2; the variable **n** ranges from 1 to 3 and, when **n** > 1, the atoms Z can be the same or different from each other, such as in divalent bridges $-CH_2-O-$, $-CH_2-S-$ and $-CH_2-Si(CH_3)_2-$.

The integer **n** ranges from 1 to 3, and it is preferably 1 or 2.

D is a delocalized π -bonded moiety, which is bound in a η^5 bonding mode to Ti; by the use of the term "delocalized π -bonded moiety" is meant an unsaturated organic moiety, such as those comprising ethylenic or acetylenic functionality, wherein the π -electrons thereof are donated to the metal to form a bond. Examples include alkene-, alkenyl-, alkyne-, alkynyl-, allyl-, polyene- and polyenyl- moieties, as well as unsaturated cyclic systems.

The D moiety is preferably a substituted or unsubstituted cyclopentadienyl group (herein referred to as Cp), optionally condensed to one or more substituted or unsubstituted, saturated, unsaturated or aromatic rings. More preferably, Cp is selected from the group consisting of cyclopentadienyl, mono-, di-, tri- and tetra-methyl cyclopentadienyl; 3-*t*-butyl-cyclopentadienyl; 3-adamantyl-cyclopentadienyl; indenyl; 2-methyl-indenyl; 4,7-dimethyl-indenyl; 3-*t*-butyl-indenyl; 3-isopropyl-indenyl; benzoindenyl; 4,5,6,7-tetrahydroindenyl; fluorenyl; tetrahydrofluorenyl; octahydrofluorenyl; N-methyl- and N-phenyl-5,10-dihydroindeno [1,2-*b*]indol-10-yl; N-methyl- and N-phenyl-5,6-dihydroindeno[2,1-*b*]indol-6-yl; azapentalen-4-yl; thiapentalen-4-yl; azapentalen-6-yl; thiapentalen-6-yl; mono-, di- and tri-methyl-azapentalen-4-yl.

According to an embodiment of the process of the invention, the Cp moiety may be a cyclopentadienyl group bearing an heteroatom substituent (such as an amino or hydrocarbyloxy groups) in the 3 position, such as 3-heteroatom substituted indenyl group, as described in WO 98/06727.

According to another embodiment, D is a cyclic or non-cyclic, non-aromatic, anionic, dienyl ligand group, as described in WO 96/08498; preferably, said dienyl ligand is a derivative of a pentadienyl, cyclohexadienyl, cyclosilahexadienyl, cycloheptadienyl, cyclooctadienyl, partially hydrogenated anthracenyl, partially hydrogenated naphthalenyl group, or a hydrocarbyl, silyl,

hydrocarbyloxy or siloxy substituted derivative thereof.

According to a most preferred embodiment, D is a (2,4-disubstituted pentadien-3-yl), (2,4-disubstituted pentadien-1-yl), (1,5-disubstituted pentadien-3-yl), (6,6-disubstituted- η^5 -cyclohexadien-3-yl), (6,6-disubstituted- η^5 -cyclosilohexadien-3-yl), (1,2,3,4,5- η -cyclohexadien-6-yl), (6-substituted-1,2,3,4,5- η -cyclohexadien-6-yl), (1,2,4,5,6,6-hexasubstituted- η^5 -cyclohexadien-3-yl), (1,1-disubstituted- η^5 -hexahydronaphthalen-4-yl), (1,1,2,3-tetrasubstituted- η^5 -hexahydronaphthalen-4-yl) or (9,9-disubstituted-10,11,12,13,14- η -1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-yl), said substituents independently in each occurrence being hydrocarbyl, silyl or a mixture thereof of up to 10 non-hydrogen atoms each.

Further D moieties suitable in the titanium complexes of formula (I) are open-pentadienyl groups, wherein the six π electron systems are not constrained to a five membered ring, as described by the same Applicant in WO 97/10248.

The group A is selected from -O-, -S-, -N(R²)- and -P(R²)-, wherein R² is defined as above; said group A is preferably -N(R²)- or -P(R²)-, i.e. an amido or phosphido group, wherein R² is preferably a linear or branched C₁-C₁₀ alkyl or a C₇-C₁₅ arylalkyl; even more preferably, R² is selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl and isomers of these alkyl radicals, norbornyl, benzyl and phenyl.

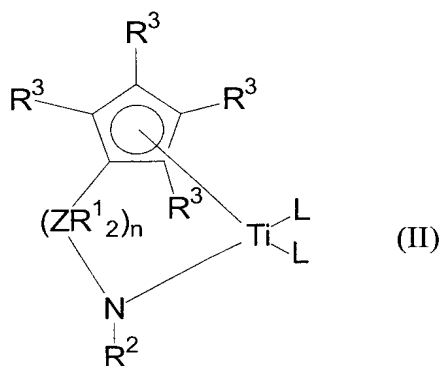
The group R² may optionally contain -OR', SR', -NR'₂ or -PR'₂ groups, wherein R' is a C₁-C₁₀ alkyl group; the presence of this addition weak neutral donor site within the chelating cyclopentadienyl ligand framework may give rise to a tridentate ligand complex; more preferably, the donor group is -OMe, -OEt or -NMe₂. When such a donor group is present on R², it is not present on the cyclopentadienyl moiety, and viceversa.

In the titanium complexes of formula (I), **p** is preferably 2 and **q** is preferably 0; X is preferably Cl or Br. The substituents L are preferably the same and are preferably selected from the group consisting of C₁-C₇ alkyl groups, C₆-C₁₄ aryl groups and C₇-C₁₄ arylalkyl groups, optionally containing one or more Si or Ge atoms; even more preferably, the substituents L are selected from the group consisting of methyl, ethyl, n-butyl, sec-butyl, phenyl, benzyl and -CH₂Si(CH₃)₃. According to a favorite embodiment of the invention, L is methyl.

Preferred dihydrocarbyl titanium complexes produced with the process of the invention are the so-called constrained geometry catalysts; by the term "constrained geometry" as used herein is meant that the titanium atom in the metal coordination complex, and also in the catalyst

resulting therefrom, is forced to greater exposure of the active catalyst site because of a specific ring structure of a ligand group including the Ti atom, wherein the metal is both bonded to an adjacent covalent moiety and held in association with the delocalized π -bonded cyclopentadienyl group through an η^5 or other π -bonding interaction. The concept of constrained geometry and specific constrain inducing ligand groups are described in EP-A-416,815; the complex must have a constrained geometry about the metal atom such that the angle at the metal between the centroid of the delocalized, substituted η -bonded moiety and the center of a constrain-inducing substituent is less than such angle in a comparative complex differing only in that said constrain-inducing substituent is replaced by hydrogen; more specifically, said angle is preferably less than 105° .

More preferably, in the present process is prepared a dihydrocarbyl titanium complex corresponding to formula (II):



wherein:

R^3 , the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated C_1 - C_{20} alkyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, C_7 - C_{20} alkylaryl or C_7 - C_{20} arylalkyl groups, optionally containing Si, Ge, O, S, N or P atoms; or two or four adjacent R^3 groups form together one or more cycles;

the R^2 group on the amido moiety has the meaning reported above, and is most preferably selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl and isomers of these alkyl radicals, norbornyl, benzyl, phenyl, p-n-butyl-phenyl, cyclohexyl and cyclododecyl; Z is C or Si; R^1 is defined as above and is most preferably selected from the group consisting of hydrogen, methyl, benzyl and phenyl; n is 1 or 2; L substituents have the meaning reported above and more preferably are methyl, neopentyl or benzyl.

Two or four adjacent R³ groups on the cyclopentadienyl group may form one or two condensed rings; therefore, the Cp moiety is preferably selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, tetrahydrofluorenyl and octahydrofluorenyl; R³ groups on the foregoing cyclopentadienyl groups are independently selected from the group consisting of hydrogen, methyl, ethyl, butyl, pentyl, hexyl and isomers of these alkyl radicals, norbornyl, benzyl and phenyl.

A non limiting list of highly preferred compounds of formula (II) include:

ethylene(tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl) titanium dimethyl
 ethylene(tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl) titanium dibenzyl
 dimethylsilanediyl(tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl) titanium dimethyl
 dimethylsilanediyl(tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl) titanium dibenzyl
 dimethylsilanediyl(methylamido)(tetramethyl- η^5 -cyclopentadienyl) titanium dimethyl
 dimethylsilanediyl(methylamido)(tetramethyl- η^5 -cyclopentadienyl) titanium dibenzyl
 dimethylsilanediyl(phenylamido)(tetramethyl- η^5 -cyclopentadienyl) titanium dimethyl
 dimethylsilanediyl(phenylamido)(tetramethyl- η^5 -cyclopentadienyl) titanium dibenzyl
 dimethylsilanediyl(benzylamido)(tetramethyl- η^5 -cyclopentadienyl) titanium dimethyl
 dimethylsilanediyl(benzylamido)(tetramethyl- η^5 -cyclopentadienyl) titanium dibenzyl
 ethylene(tert-butylamido)(η^5 -cyclopentadienyl) titanium dimethyl
 ethylene(tert-butylamido)(η^5 -cyclopentadienyl) titanium dibenzyl
 dimethylsilanediyl(tert-butylamido)(η^5 -cyclopentadienyl) titanium dimethyl
 dimethylsilanediyl(tert-butylamido)(η^5 -cyclopentadienyl) titanium dibenzyl
 dimethylsilanediyl(methylamido)(η^5 -cyclopentadienyl) titanium dimethyl
 dimethylsilanediyl(methylamido)(η^5 -cyclopentadienyl) dibenzyl
 dimethylsilanediyl(tert-butylamido)(indenyl) titanium dimethyl
 dimethylsilanediyl(tert-butylamido)(indenyl) titanium dibenzyl
 dimethylsilanediyl (benzylamido)(indenyl) titanium dimethyl and
 dimethylsilanediyl(benzylamido)(indenyl) titanium dibenzyl.

The process according to the present invention comprises the following steps, carried out in one reactor:

(1) reacting a ligand of formula (H-D)(ZR¹_m)_n(A-H) with about (2 + p) molar equivalents of a

compound of formula L_jB or $LMgX$, wherein D, A, Z, R^1 , **m**, **n**, **p**, X and L have the meaning reported above; B is an alkaline or alkaline-earth metal; **j** is 1 or 2, **j** being equal to 1 when B is an alkaline metal, and **j** being equal to 2 when B is an alkaline-earth metal; and (2) reacting the product obtained from step (1) with about 1 molar equivalent of a compound of formula TiX_4 , wherein X has the meaning reported above.

The hydrocarbyl titanium complexes of formulae (I) and (II) can be finally isolated from the reaction mixture obtained in step (2) and optionally purified according to standard procedures. Said process allows to obtain the hydrocarbyl titanium complexes of formulae (I) and (II) in very high yields, by means of a very practical and convenient one-pot reaction.

Surprisingly, it has been found that when reacting a suitable ligand with about 4 molar equivalents of a compound of formula L_jB or $LMgX$ and about 1 molar equivalent of a compound of formula TiX_4 , the desired dihydrocarbyl titanium complexes are obtained, in high yield and high purity, with a one-pot reaction. Analogously, when reacting a suitable ligand with about 3 molar equivalents of a compound of formula L_jB or $LMgX$ and about 1 molar equivalent of a compound of formula TiX_4 , the desired monohydrocarbyl titanium complexes are obtained, in high yield and high purity, with a one-pot reaction.

Moreover, it is not observed a significant reduction of Ti(IV) to Ti(III), that would lead to very poor reaction yields or would render necessary a further oxidation step; this is completely unexpected in the light of the processes reported in prior art literature, as already stressed above.

This new process typically provides the complexes of formulae (I) and (II) in yields of 60% and higher; the product complexes can be readily isolated in high purity by filtration, without the need of laborious purification procedures.

In the reactant TiX_4 , the substituents X are preferably the same and are selected from the group consisting of -Cl, -Br, -OMe, -OEt, -OPr, -OBu and -OBz; said reactant is preferably selected from the group consisting of $TiCl_4$, $Ti(OEt)_4$, $Ti(OPr)_4$ and $Ti(OBz)_4$; it can be used even in the form of a stabilized derivative, such as an etherate complex of TiX_4 .

L_jB and $LMgX$ are alkylating agents, wherein L is preferably a C_1 - C_8 alkyl group, a C_6 - C_{14} aryl group or a C_7 - C_{14} alkylaryl group, optionally substituted with Si or Ge, and more preferably L is selected from the group consisting of methyl, ethyl, n-butyl, sec-butyl, phenyl, benzyl and $-CH_2Si(CH_3)_3$; even more preferably, L is methyl.

In the compound L_jB , B is an alkaline or alkaline-earth metal, and preferably Li or Mg; j can be 1 or 2, as already reported.

The compound $LMgX$ is a Grignard reagent, wherein Mg is magnesium and L and X have the meaning reported above; X is preferably Cl or Br.

According to a preferred embodiment of the process of the invention, said alkylating agent is methyllithium.

The molar ratio of the compound of formula L_jB or $LMgX$ to the ligand of formula $(H-D)(ZR^1_m)_n(A-H)$ can vary within wide limits; an improved process for obtaining dihydrocarbyl complexes of formula (I), wherein $p = 2$ and $q = 0$, is obtained at ratios of about 4:1 and higher; an improved process for obtaining monohydrocarbyl complexes of formula (I), wherein $p = 1$ and $q = 1$, is obtained at ratios of about 3:1.

The molar ratio of the compound of formula TiX_4 to the ligand of formula $(H-D)(ZR^1_m)_n(A-H)$ is preferably about 1:1.

According to a preferred embodiment, the process of the invention is carried out in an aprotic solvent, either polar or apolar; said aprotic solvent is preferably an aromatic or aliphatic hydrocarbon or an ether, and more preferably it is selected from the group consisting of benzene, toluene, pentane, hexane, heptane, cyclohexane, diethylether, tetrahydrofurane and mixtures thereof.

According to another embodiment of the process of the invention, in step (1) said ligand $(H-D)(ZR^1_m)_n(A-H)$ is previously dissolved in an aprotic solvent and to the resulting solution is added the alkylating agent L_jB or $LMgX$; this addition is preferably carried out at a temperature ranging from -80°C to $+50^\circ\text{C}$, and more preferably from -50°C to $+30^\circ\text{C}$. The alkylating agent is preferably added in the form of a solution in one of the above mentioned aprotic solvents.

The thus obtained reaction mixture is preferably allowed to react, under stirring, at a temperature comprised between -80°C and $+50^\circ\text{C}$, more preferably between -50°C and $+30^\circ\text{C}$, and even more preferably at room temperature.

Before the reaction with TiX_4 in step (2), the mixture obtained from step (1) is preferably cooled to a temperature ranging from -80°C to $+50^\circ\text{C}$, and more preferably from -80°C to room temperature; TiX_4 is then added to the cooled mixture, in the form of a solution in one of the above mentioned aprotic solvents, preferably pentane.

The reaction mixture is then allowed to react at a temperature comprised between -80°C and

+50°C, more preferably between -50°C and +30°C, and even more preferably at room temperature.

The thus obtained titanium complexes of formula (I) and (II) can be isolated according to common procedures known in the state of the art.

The titanium complexes obtained with the process according to the present invention are useful in addition polymerization processes wherein, in association with an activating cocatalyst, they are contacted with one or more addition polymerizable monomers.

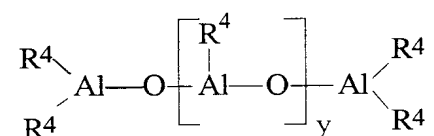
Addition polymerizable monomers include ethylenically unsaturated monomers, conjugated or non-conjugated dienes and polyenes. The hydrocarbyl titanium complexes are particularly useful in homo and co-polymerization of α -olefins of formula $\text{CH}_2=\text{CHR}$, wherein R is hydrogen or a $\text{C}_1\text{-C}_{20}$ alkyl, such as propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene and 1-octene.

Other preferred addition polymerizable monomers include styrene, halo or alkyl substituted styrene, vinylbenzocyclobutane, 1,4-hexadiene, ethyldenenorbornene, cyclopentene and norbornene.

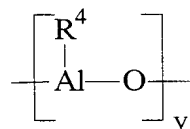
As reported above, the hydrocarbyl titanium complexes obtained with the process of the invention form suitable polymerization catalytic systems in association with activating cocatalysts, such as the ones described in EP-A-416,815 and WO 92/10360. The term "activating cocatalyst" as used herein refers to a secondary component of the catalyst system able to cause the metal-containing complex to become effective as an addition polymerization catalyst or alternatively to balance the ionic charge of a catalytically activated species. Examples of the foregoing activating cocatalysts for use herein include alumoxanes, aluminum alkyls, aluminum halides, aluminum alkylhalides, Lewis acids, ammonium salts, non-interfering oxidizing agents and mixtures thereof.

Preferably the ratio of the hydrocarbyl titanium complex and cocatalyst on a molar basis is from about 1:0.1 to about 1:10,000, and more preferably from 1:1 to 1:1,000.

Suitable activating cocatalysts are linear alumoxanes having the following formula:



wherein R^4 is selected from the group consisting of halogen, linear or branched, saturated or unsaturated C_1 - C_{20} alkyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, C_7 - C_{20} alkylaryl and C_7 - C_{20} arylalkyl radicals, optionally containing Si and Ge atoms, and y ranges from 0 to 40; R^4 is preferably methyl, ethyl, isobutyl or 2,4,4-trimethyl-pentyl;
or cyclic alumoxanes having the following formula:



wherein R^4 has the meaning herein described and y is an integer ranging from 2 to 40.

Examples of alumoxanes suitable as activating cocatalysts in the catalysts according to the present invention are methylalumoxane (MAO), tetra-isobutyl-alumoxane (TIBAO), tetra-2,4,4-trimethylpentylalumoxane (TIOAO) and tetra-2-methyl-pentylalumoxane. Mixtures of different alumoxanes can also be used.

Suitable activating cocatalysts are also the products of the reaction between water and an organometallic aluminum compound, preferably of formula AlR^4_3 or $Al_2R^4_6$, wherein R^4 has the meaning reported above. Particularly suitable are the organometallic aluminum compounds of formula (II) described in EP-A-575,875, those of formula (II) described in WO 96/02580, those described in the WO 99/21899 and in the European app. no. 99203110.4. Non-limiting examples of organometallic aluminum compounds of formula AlR^4_3 or $Al_2R^4_6$ are:

tris(methyl)aluminum,	tris(isobutyl)aluminum,
tris(isooctyl)aluminum,	bis(isobutyl)aluminum hydride,
methyl-bis(isobutyl)aluminum, dimethyl(isobutyl)aluminum,	
tris(isohexyl)aluminum,	tris(benzyl)aluminum,
tris(tolyl)aluminum,	tris(2,4,4-trimethylpentyl)aluminum,
bis(2,4,4-trimethylpentyl)aluminum hydride, isobutyl-bis(2-phenyl-propyl)aluminum,	
diisobutyl-(2-phenyl-propyl)aluminum, isobutyl-bis(2,4,4-trimethyl-pentyl)aluminum,	
diisobutyl-(2,4,4-trimethyl-pentyl)aluminum, tris(2,3-dimethyl-hexyl)aluminum,	
tris(2,3,3-trimethyl-butyl)aluminum,	tris(2,3-dimethyl-butyl)aluminum,
tris(2,3-dimethyl-pentyl)aluminum,	tris(2-methyl-3-ethyl-pentyl)aluminum,

tris(2-ethyl-3-methyl-butyl)aluminum, tris(2-ethyl-3-methyl-pentyl)aluminum, tris(2-isopropyl-3-methyl-butyl)aluminum and tris(2,4-dimethyl-heptyl)aluminum.

Particularly preferred aluminum compounds are trimethylaluminum (TMA), tris(2,4,4-trimethylpentyl) aluminum (TIOA), triisobutylaluminum (TIBA), tris(2,3,3-trimethyl-butyl)aluminum and tris(2,3-dimethyl-butyl)aluminum.

Mixtures of different organometallic aluminum compounds can also be used.

Further suitable activating cocatalysts are those compounds capable of forming an alkylmetallocene cation; preferably, said compounds have formula Y^+Z^- , wherein Y^+ is a Brønsted acid capable of donating a proton and of reacting irreversibly with a substituent X of the compound of formula (I), and Z^- is a compatible non-coordinating anion, capable of stabilizing the active catalytic species which result from the reaction of the two compounds, and which is sufficiently labile to be displaceable by an olefinic substrate. Preferably, the Z^- anion comprises one or more boron atoms. More preferably, the anion Z^- is an anion of formula $BAr_4^{(-)}$, wherein the Ar substituents, the same or different from each other, are aryl radicals such as phenyl, pentafluorophenyl, bis(trifluoromethyl)phenyl. Tetrakis-pentafluorophenyl-borate is particularly preferred. Moreover, compounds of formula BAr_3 can be conveniently used.

The polymerization processes may be carried out in liquid phase, optionally in the presence of an inert hydrocarbon solvent either aromatic (e.g. toluene) or aliphatic (e.g. propane, hexane, heptane, isobutane, cyclohexane and 2,2,4-trimethylpentane), or in the gas phase.

The polymerization is conducted according to known techniques for Ziegler-Natta or Kaminsky-Sinn type polymerization, at a temperature generally ranging from about -30°C to about 250°C , and preferably from 20 to 150°C , at reduced, elevated or atmospheric pressures.

The molecular weight of the polymers can be varied by changing the type or the concentration of the catalytic components or by using molecular weight regulators, for example hydrogen.

The catalyst may be used as it is or supported on a suitable organic or inorganic support, to provide a heterogeneous supported catalyst.

The following examples are given for illustrative and not limiting purposes.

GENERAL PROCEDURES AND CHARACTERIZATIONS

All operations were performed under nitrogen by using conventional Schlenk-line techniques. Solvents were purified by degassing with nitrogen and passing over activated

alumina and subsequently stored under nitrogen.

BuLi (Aldrich), Me_2SiCl_2 (Aldrich), NH_2^tBu (Aldrich), MeLi (Acros), piperidine (Aldrich), TiCl_4 and ZrCl_4 were used as received.

Indene (Aldrich) was purified by passing over activated alumina and subsequently stored under nitrogen.

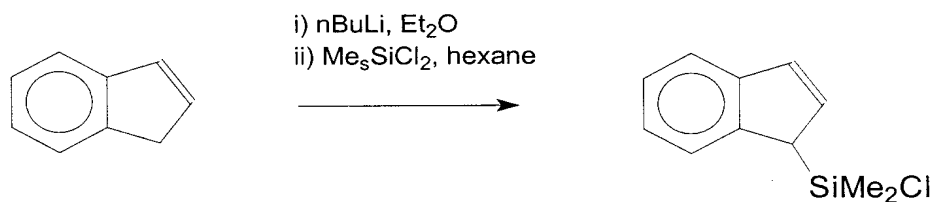
All compounds were analyzed by ^1H -NMR (CDCl_3 , referenced against the peak of the residual CHCl_3 at 7.25 ppm) or ^{13}C -NMR (Broad Band Decoupling, CDCl_3 , referenced against the middle peak of CDCl_3 at 77.00 ppm), by using a AC200 Bruker spectrometer, operating at 200.13 MHz for ^1H and 50.323 MHz for ^{13}C . All NMR solvents were dried over P_4O_{10} and distilled before use. Preparation of the samples was carried out under nitrogen, using standard inert atmosphere techniques.

GC-MS analysis were carried out on a HP5890 series 2 gas-chromatograph and a HP5970 mass spectrometer.

EXAMPLE 1

Synthesis of dimethylsilanediyl(tert-butylamido)(indenyl) titanium dimethyl

(a) Synthesis of (indenyl)(dimethyl)chlorosilane $\text{IndSiMe}_2\text{Cl}$



A solution of $n\text{-BuLi}$ 2.5 M in hexane (37.5 ml, 93.75 mmoles) was added dropwise to a solution of indene (purity 90 %, 11 ml, 84.9 mmoles) in 60 ml Et_2O , maintained under stirring at -78°C (molar ratio indene: $n\text{-BuLi}$ = 1:1.1). At the end of the addition, the yellow slurry was allowed to reach room temperature and the reaction mixture was left under stirring for 4 hours to give an orange solution. The solvent was evaporated under reduced pressure to give a yellow solid, which was taken up in $n\text{-hexane}$ (75 ml), thus obtaining a milky suspension, that was maintained under stirring for 5 minutes. Said suspension was filtered and the lithium salt of indene was separated as a white solid residue, which was washed with $n\text{-hexane}$ (3x20 ml) in order to remove the unreacted indene.

The solid residue was re-suspended in n-hexane (40 ml) and added to a stirred solution of Me_2SiCl_2 (15.6 ml, 136.8 mmol; $\text{Me}_2\text{SiCl}_2/\text{indLi} = 1.5$) in hexane (50 ml), previously cooled to -78°C . At the end of the addition, the mixture was allowed to reach room temperature and was maintained under stirring overnight.

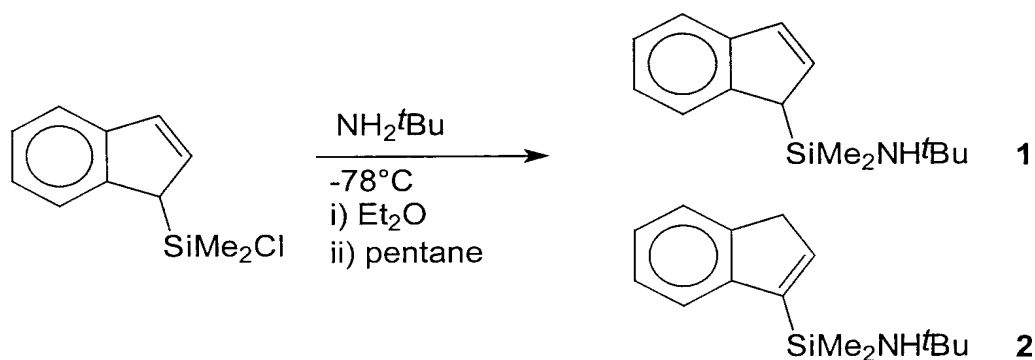
The suspension was then filtered, thus removing the solid residue LiCl , and the yellow solution obtained was brought to dryness in vacuo to yield a light yellow oil (16.5 g) of $\text{IndSiMe}_2\text{Cl}$, free from its vinylic isomer (yield 89%).

The product contained also a small quantity of the byproduct $\text{Me}_2\text{SiInd}_2$ (rac/meso = 1:1.2; about 5%).

$^1\text{H-NMR}$ (CDCl_3 , 7.25 ppm): $\delta = 0.21$ (s, 3 H, Si-CH_3); 0.26 (s, 3 H, Si-CH_3); 3.77 (br-t, $J = 1.87$ Hz, 1H, Cp-H); 6.68 (dd, $J = 5.39, 1.87$ Hz, 1H, Cp-H); 7.03 (ddd, $J = 5.39, 1.87, 0.62$ Hz, 1 H, Cp-H); $7.19 - 7.36$ (m, 2H, Ar), $7.48-7.52$ (m, 1H, Ar), $7.57-7.61$ (m, 1H, Ar).

GC-MS: $[m/z] = 208$ [M^+], 115 [$\text{M}^+ - \text{SiMe}_2\text{Cl}$], 93 [$\text{M}^+ - \text{C}_9\text{H}_7$].

(b) Synthesis of (tert-butylamino)(dimethyl)(indenyl)silane *IndSiMe₂NH^tBu*



A solution of $\text{IndSiMe}_2\text{Cl}$ (5.6 g, 26.8 mmol) in Et_2O (10 ml) was added dropwise, under continuous stirring, to a solution of 6.6 ml of $t\text{-BuNH}_2$ (62.9 mmol, $t\text{-BuNH}_2/\text{IndSiMe}_2\text{Cl} = 2.3$) in Et_2O (50 ml), cooled to -78°C . At the end of the addition, the mixture was allowed to reach room temperature and was left under stirring for 24 hours to give a white milky suspension. The solvent was evaporated under reduced pressure and the residue was extracted with n-pentane (40 ml). The suspension was filtered in order to remove the white ammonium salt $t\text{-BuH}_3\text{NCl}$ from the soluble product; the filtrate was concentrated in vacuo to give a light lemon yellow oil (5.46 g, 83%).

GC-MS, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ analysis of the product showed the formation of $\text{IndSiMe}_2\text{NH-}t\text{Bu}$ as a mixture of two isomers (allyl isomer 1 = 75%; vinyl isomer 2 = 25%), with a total yield of 88%.

$^1\text{H-NMR}$ (CDCl_3 , 7.25 ppm): Isomer 1: δ = -0.01 (s, 3 H, Si-CH_3); 0.03 (s, 3 H, Si-CH_3); 0.72 (br-s, 1 H, N-H); 1.28 (s, 9 H, $t\text{-Bu}$); 3.68 (br-t, J = 1.87 Hz 1 H, Cp-H-1); 6.76 (dd, J = 5.39, 1.87 Hz, 1 H, Cp-H); 6.98 (ddd, J = 5.39, 1.87, 0.62 Hz, 1 Cp-H); 7.15 – 7.40 (m, 2 H, Ar), 7.5-7.61 (m, 2H, Ar).

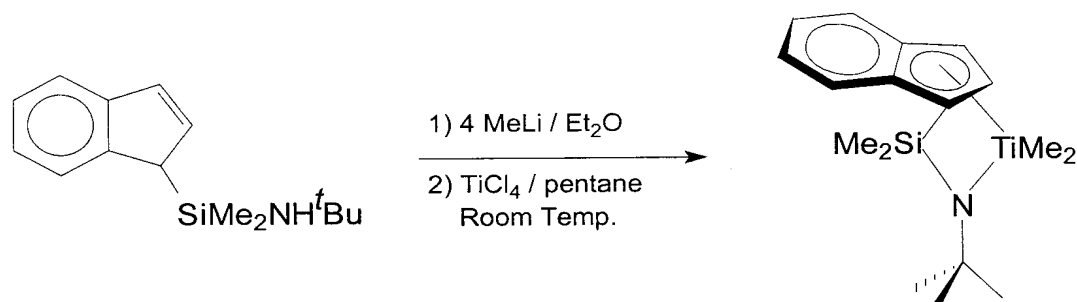
$^1\text{H-NMR}$ (CDCl_3 , 7.25 ppm): Isomer 2: δ = 0.44 (s, 6 H, $\text{Si}(\text{CH}_3)_2$); 0.9 (br-s, 1 H, N-H); 1.22 (s, 9 H, $t\text{-Bu}$); 3.47 (br-m, 2 H, Cp-H-1); 6.87 (t, J = 1.87 Hz, 1H, Cp-H-2), 3 aromatic protons overlap with those of the allylic isomer; 7.77 (d, 1H, Ar).

$^{13}\text{C-NMR}$ (CDCl_3 , 77 ppm): Isomer 1: δ = -0.60 (s, $\text{Si}(\text{CH}_3)_2$); 0.16 (s, $\text{Si}(\text{CH}_3)_2$); 34.28 (s, $\text{N-C}(\text{CH}_3)_3$); 50.00 (s, C1); 50.08 (s, $\text{N-C}(\text{CH}_3)_3$); 121.26 – 126.31 (C4-9); 129.12 (s, C3); 135.46 (s, C2).

$^{13}\text{C-NMR}$ (CDCl_3 , 77 ppm): Isomer 2: δ = 1.82 (s, $\text{Si}(\text{CH}_3)_2$); 34.03 (s, $\text{N-C}(\text{CH}_3)_3$); 41.02 (s, CH_2); 145.60 (s, C2).

GC-MS: $[m/z] = 245 [M^+]$, $130 [M^+ - \text{C}_9\text{H}_7]$, $115 [M^+ - \text{SiMe}_2\text{NH}^t\text{Bu}]$.

(c) Synthesis of dimethylsilanediyl(tert-butylamido)(indenyl) titanium dimethyl $[\text{IndSiMe}_2\text{N}^t\text{Bu}]\text{TiMe}_2$



11.30 ml of a solution of MeLi 1.6 M in Et_2O (18.04 mmoles) were slowly added at -78°C to a solution containing 1.08g (4.40 mmoles) of (tert-butylamino)(dimethyl) (indenyl)silane $\text{IndSiMe}_2\text{NH}^t\text{Bu}$ in 23 ml of Et_2O (the molar ratio $\text{IndSiMe}_2\text{NH}^t\text{Bu} / \text{MeLi} = 1:4.2$). During the addition an increasing turbidity developed with final formation of a yellow suspension. The mixture was stirred for 2 hours at room temperature.

To the suspension was slowly and cautiously added, at room temperature, a mixture of 0.5 ml of TiCl_4 (4.40 mmoles) in 23 ml n-pentane (the molar ratio $\text{IndSiMe}_2\text{NH}^t\text{Bu}/\text{TiCl}_4 = 1:1$).

The mixture turned quickly to dark green color with a consistent development of gas; at the end of the addition a brown suspension was obtained. Such suspension was stirred overnight. The reaction mixture was then brought to dryness under reduced pressure. The dark solid was extracted with 60 ml of toluene and then the filtrate was evaporated to dryness under reduced pressure to give 0.99 g (70% yield) of a gray-black solid. Its $^1\text{H-NMR}$ analysis confirmed the formation of $[\text{IndSiMe}_2\text{N}^t\text{Bu}]\text{TiMe}_2$.

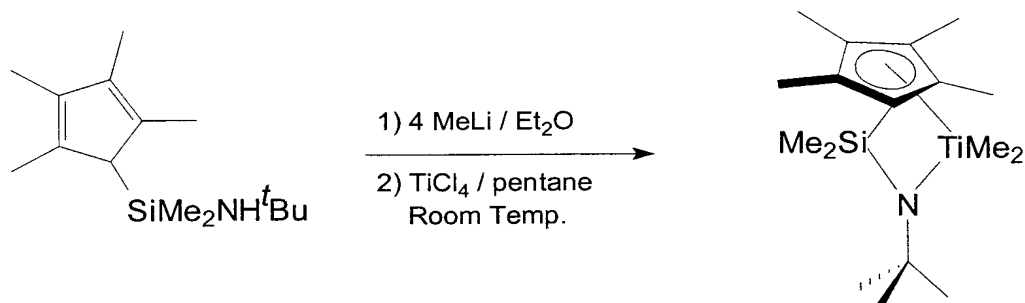
$^1\text{H-NMR}$ (CDCl_3 , 7.25 ppm): $\delta = -0.553$ (s, 3H, $\text{Ti}(\text{CH}_3)_2$); 0.479 (s, 3H, $\text{Si}(\text{CH}_3)_2$); 0.535 (s, 3H, $\text{Si}(\text{CH}_3)_2$); 0.706 (s, 3H, $\text{Ti}(\text{CH}_3)_2$); 6.220 (d, 1H, H2, $^3J_{\text{HH}} = 3$ Hz); 7.048-7.129 (m, 1H, arom); 7.263-7.344 (m, 2H, arom and H3); 7.457-7.504 (m, 1H, arom); 7.744-7.791 (m, 1H, arom).

$^1\text{H-NMR}$ (C_6D_6 , 7.16 ppm): $\delta = -0.15$ (q, $J = 0.48$ Hz, 3H, Ti-CH_3); 0.36 (s, 3H, Si-CH_3); 0.53 (s, 3H, Si-CH_3); 0.82 (q, $J = 0.48$ Hz, 3H, Ti-CH_3); 1.44 (s, 9H, $t\text{-Bu}$); 6.05 (d, $J = 3.21$, 1H, Cp-H2); 6.88 (ddd, $J = 8.50, 6.64, 1.04$ Hz, 1H, Ar-H6); 7.01 (dd, $J = 3.21, 0.83$ Hz, 1H, Cp-H3); 7.07 (ddd, $J = 8.50, 6.64, 1.04$ Hz, 1H, Ar-H5); 7.46 (dq, $J = 8.50, 1.04$ Hz, 1H, Ar-H7); 7.48 (dt, $J = 8.50, 1.04$ Hz, 1H, Ar-H4).

The reaction yield of dimethylsilanediyl(tert-butylamido)(indenyl) titanium dimethyl, obtained with the one-step process according to the present invention (70%), is much higher than the one obtainable with the two reaction steps according to the literature procedures (lower than 42%), as already reported in the prior art description.

EXAMPLE 2

Synthesis of dimethylsilanediyl(tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl) titanium dimethyl



20.9 ml of a solution of MeLi 1.6 M in Et₂O (33.52 mmoles) were slowly added at -78°C to a solution containing 2.0g (7.98 mmoles) of (tert-butylamino)(dimethyl)(tetramethylcyclopentadi-2,4-enyl)silane Me₄CpSiMe₂NH*t*-Bu in 43 ml of Et₂O (the molar ratio Me₄CpSiMe₂NH*t*-Bu/MeLi = 1:4.2). During the addition, an increasing turbidity developed, with final formation of a white dense suspension. The mixture was allowed to warm to room temperature and then stirred for 2 hours.

To said suspension was added, at room temperature, a mixture of 0.88 ml of TiCl₄ (7.98 mmoles) in 43 ml n-pentane (the molar ratio Me₄CpSiMe₂NH*t*-Bu/TiCl₄ = 1:1). The mixture turned quickly to a dark green color with a consistent development of gas; at the end of the addition a black suspension was obtained, which was stirred at room temperature overnight.

The reaction mixture was then brought to dryness under reduced pressure. The dark solid was extracted with 120 ml of toluene and then the filtrate was evaporated to dryness under reduced pressure to give 1.51 g (60% yield) of a black solid. ¹H-NMR showed the presence of chemically pure dimethylsilanediyl(tert-butylamido)(tetramethyl-η⁵-cyclopentadienyl) titanium dimethyl.

¹H NMR (δ, ppm, C₆D₆; ref. C₆D₅H at 7.16 ppm): 0.43 (s, 6H, Si-CH₃), 0.49 (s, 6H, Ti-CH₃), 1.56 (s, 9H, *t*-Bu), 1.85 (s, 6H, Cp-CH₃), 1.96 (s, 6H, Cp-CH₃).

The reaction yield of dimethylsilanediyl(tert-butylamido)(tetramethyl-η⁵-cyclopentadienyl) titanium dimethyl, obtained with the one-step process according to the present invention (60%), is much higher than the one obtainable with the two reaction steps according to the literature procedures (lower than 32%), as already reported in the prior art description.

CLAIMS

1. A process for the preparation of titanium complexes of formula (I):



wherein:

$(ZR^1_m)_n$ is a divalent group bridging D and A; Z is selected from the group consisting of C, Si, Ge, N, P and B; the R^1 groups, the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated C_1 - C_{20} alkyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, C_7 - C_{20} alkylaryl and C_7 - C_{20} arylalkyl groups, or two R^1 groups form together a cycle; m is 1 or 2; n is an integer ranging from 1 to 3;

D is a delocalized π -bonded moiety, which is bound in a η^5 bonding mode to Ti;

A is a divalent anionic group selected from $-O-$, $-S-$, $-N(R^2)-$ and $-P(R^2)-$, wherein R^2 is hydrogen, a linear or branched, saturated or unsaturated C_1 - C_{20} alkyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, C_7 - C_{20} alkylaryl or C_7 - C_{20} arylalkyl, optionally containing $-OR'$, $-SR'$, $-NR'_2$ or $-PR'_2$ groups, wherein R' is a C_1 - C_{10} alkyl group;

Ti is titanium;

the substituents L, same or different from each other, are monoanionic sigma ligands selected from the group consisting of linear or branched, saturated or unsaturated C_1 - C_{20} alkyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, C_7 - C_{20} alkylaryl and C_7 - C_{20} arylalkyl groups, optionally containing one or more Si or Ge atoms;

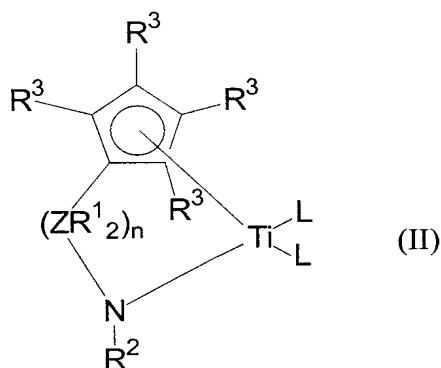
X is halogen or $-OR'$, wherein R' is a C_1 - C_{10} alkyl group;

p is 1 or 2; q is 0 or 1, and $p + q = 2$;

said process being characterized by comprising the following steps:

- (1) reacting a ligand of formula $(H-D)(ZR^1_m)_n(A-H)$ with about $(2 + p)$ molar equivalents of a compound of formula L_jB or $LMgX$, wherein D, A, Z, R^1 , m , n , p , X and L have the meaning reported above; B is an alkaline or alkaline-earth metal; j is 1 or 2, j being equal to 1 when B is an alkaline metal, and j being equal to 2 when B is an alkaline-earth metal; and
 - (2) reacting the product obtained from step (1) with about 1 molar equivalent of a compound of formula TiX_4 , wherein X has the meaning reported above.
2. The process according to claim 1, wherein $(ZR^1_m)_n$ is selected from the group consisting of

- CR^1_2 , $(CR^1_2)_2$, $(CR^1_2)_3$, $CR^1=CR^1$, SiR^1_2 , $(SiR^1_2)_2$, $CR^1_2-SiR^1_2$, GeR^1_2 , NR^1 , PR^1 and BR^1 , R^1 having the meaning reported in claim 1.
3. The process according to claim 2, wherein $(ZR^1_m)_n$ is selected from the group consisting of $Si(CH_3)_2$, $SiPh_2$, CH_2 , $(CH_2)_2$, $(CH_2)_3$ and $C(CH_3)_2$.
 4. The process according to claim 1, wherein D is a substituted or unsubstituted cyclopentadienyl group, optionally condensed to one or more substituted or unsubstituted, saturated, unsaturated or aromatic rings.
 5. The process according to claim 4, wherein D is selected from the group consisting of cyclopentadienyl, mono-, di-, tri- and tetra-methyl cyclopentadienyl; 3-*t*butyl-cyclopentadienyl; 3-adamantyl-cyclopentadienyl; indenyl; 2-methyl-indenyl; 4,7-dimethyl-indenyl; 3-*t*butyl-indenyl; 3-isopropyl-indenyl; benzoindenyl; 4,5,6,7-tetrahydroindenyl; fluorenyl; tetrahydrofluorenyl; octahydrofluorenyl; N-methyl- and N-phenyl-5,10-dihydroindeno [1,2-b]indol-10-yl; N-methyl- and N-phenyl-5,6-dihydroindeno[2,1-b]indol-6-yl; azapentalene-4-yl; thiapentalen-4-yl; azapentalen-6-yl; thiapentalen-6-yl; mono-, di- and tri-methyl-azapentalen-4-yl.
 6. The process according to claim 1, wherein said divalent anionic group A is $-N(R^2)-$ or $-P(R^2)$ and $-R^2$ is selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl and isomers of these alkyl radicals, norbornyl, benzyl and phenyl.
 7. The process according to claim 1, wherein **p** is 2, **q** is 0 and the substituents L are the same and are selected from the group consisting of methyl, ethyl, n-butyl, sec-butyl, phenyl, benzyl and $-CH_2Si(CH_3)_3$.
 8. The process according to claim 1, wherein said titanium complex corresponds to formula (II):



wherein:

R^1 , R^2 and L have the meaning reported in claim 1; Z is C or Si; n is 1 or 2;

R^3 , the same or different from each other, are selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated C_1 - C_{20} alkyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, C_7 - C_{20} alkylaryl or C_7 - C_{20} arylalkyl groups, optionally containing Si, Ge, O, S, N or P atoms, or two or four adjacent R^3 groups form together one or more cycles.

9. The process according to claim 8, wherein R^1 is selected from the group consisting of hydrogen, methyl, benzyl and phenyl; R^2 is selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl and isomers of these alkyl radicals, norbornyl, benzyl, phenyl, p-n-butyl-phenyl, cyclohexyl and cyclododecyl; R^3 is selected from the group consisting of hydrogen, methyl, ethyl, butyl, pentyl, hexyl and isomers of these alkyl radicals, norbornyl, benzyl and phenyl, or two or four adjacent R^3 groups form one or two condensed rings; the substituents L are the same and are selected from the group consisting of methyl, neopentyl and benzyl.
10. The process according to claim 1, wherein in the reactant TiX_4 , the substituents X are the same and are selected from the group consisting of -Cl, -Br, -OMe, -OEt, -OPr, -OBu and -OBz.
11. The process according to claim 1 wherein, in the compounds of formulae L_jB and $LMgX$, L is selected from the group consisting of methyl, ethyl, n-butyl, sec-butyl, phenyl, benzyl and $-CH_2Si(CH_3)_3$; j is 1 or 2; B is Li or Mg; and X is Cl or Br.
12. The process according to claim 11, wherein L is methyl.
13. The process according to claim 1, characterized by being carried out in an aprotic solvent.
14. The process according to claim 15, wherein said aprotic solvent is selected from the group consisting of benzene, toluene, pentane, hexane, heptane, cyclohexane, diethylether, tetrahydrofurane and mixtures thereof.
15. The process according to claim 1, wherein in step (1), said ligand $(H-D)(ZR^1_m)_n(A-H)$ is first dissolved in an aprotic solvent and to the resulting solution is added L_jB or $LMgX$, and finally TiX_4 is added.

INTERNATIONAL SEARCH REPORT

Intern 1al Application No

PCT/EP 00/00747

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07F17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 512 693 A (ROSEN, ROBERT K. ET AL) 30 April 1996 (1996-04-30) example 3	1
A	--- HERRMANN, WOLFGANG A. ET AL: "Synthesis and characterization of bridged half-sandwich amides of titaniu and zirconium" J. ORGANOMET. CHEM. (1994), 482(1-2), 169-81 , XP002135076 cited in the application the whole document --- -/--	1

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

13 April 2000

Date of mailing of the international search report

27/04/2000

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Rinkel, L

INTERNATIONAL SEARCH REPORT

Intern: al Application No

PCT/EP 00/00747

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEN, YOU-XIAN ET AL: ""Constrained Geometry" Dialkyl Catalysts. Efficient Syntheses, C-H Bond Activation Chemistry, Monomer-Dimer Equilibration, and.alpha.-Olefin Polymerization Catalysis" ORGANOMETALLICS (1997), 16(16), 3649-3657 , XP002135077 cited in the application the whole document	1
X,P	WO 99 36427 A (MONTELL TECHNOLOGY COMPANY B.V.) 22 July 1999 (1999-07-22) cited in the application the whole document	1

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/EP 00/00747

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5512693 A	30-04-1996	AT 174032 T	15-12-1998
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		AU 4199096 A	26-06-1996
		BR 9510081 A	14-07-1998
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		FI 972432 A	06-06-1997
		JP 10510262 T	06-10-1998
		NO 972621 A	06-06-1997
		WO 9617857 A	13-06-1996
WO 9936427 A	22-07-1999	EP 0979232 A	16-02-2000

DERWENT-ACC-NO: 2001-191232**DERWENT-WEEK:** 200453*COPYRIGHT 2008 DERWENT INFORMATION LTD*

TITLE: Preparation of titanium complexes,
useful as catalyst components in the
polymerization of olefins, by
contacting a titanium reactant and a
dilithium salt of a cyclopentadienyl
ligand

INVENTOR: RESCONI L

PATENT-ASSIGNEE: BASELL POLYOLEFINE GMBH[BASE] ,
BASELL TECHNOLOGY CO BV[BASE]

PRIORITY-DATA: 1999EP-201769 (June 4, 1999)**PATENT-FAMILY:**

PUB-NO	PUB-DATE	LANGUAGE
WO 0075151 A1	December 14, 2000	EN
EP 1102778 A1	May 30, 2001	EN
KR 2001072229 A	July 31, 2001	KO
CN 1345325 A	April 17, 2002	ZH
JP 2003501436 W	January 14, 2003	JA
EP 1102778 B1	April 2, 2003	EN
DE 60001902 E	May 8, 2003	DE
US 6774253 B1	August 10, 2004	EN

DESIGNATED-STATES: CN JP KR RU US AT BE CH CY DE DK ES
FI FR GB GR IE IT LU MC NL PT SE AT
BE CH CY DE DK ES FI FR GB GR IE IT
LI LU MC NL PT SE CH DE FR GB IT LI

APPLICATION-DATA:

PUB-NO	APPL- DESCRIPTOR	APPL-NO	APPL-DATE
WO2000075151A1	N/A	2000WO- EP00747	January 31, 2000
CN 1345325A	N/A	2000CN- 801534	January 31, 2000
DE 60001902E	N/A	2000DE- 601902	January 31, 2000
EP 1102778A1	N/A	2000EP- 901140	January 31, 2000
EP 1102778B1	N/A	2000EP- 901140	January 31, 2000
EP 1102778A1	N/A	2000WO- EP00747	January 31, 2000
CN 1345325A	N/A	2000WO- EP00747	January 31, 2000
JP2003501436W	N/A	2000WO- EP00747	January 31, 2000
EP 1102778B1	N/A	2000WO- EP00747	January 31, 2000
DE 60001902E	N/A	2000WO- EP00747	January 31, 2000
US 6774253B1	N/A	2000WO- EP00747	January 31, 2000
JP2003501436W	N/A	2001JP- 502432	January 31, 2000
KR2001072229A	N/A	2001KR- 701474	February 2, 2001
US 6774253B1	Based on	2001US- 762125	February 2, 2001

INT-CL-CURRENT:

TYPE	IPC DATE
CIPP	C07F7/28 20060101
CIPS	C07F17/00 20060101
CIPS	C07F19/00 20060101

ABSTRACTED-PUB-NO: WO 0075151 A1

BASIC-ABSTRACT:

NOVELTY - Titanium complexes are prepared by contacting a titanium reactant and a dilithium salt of a cyclopentadienyl ligand.

DESCRIPTION - Preparation of titanium complexes of formula (I) involves

(i) reacting a ligand of formula $(H-D)(ZR_1m)_n(AH)$ with $(2 + p)$ molar equivalents of compound of formula LjB or $LMgX$, and

(ii) reacting the product with 1 molar equivalent of a compound of formula TiX_4 .

$(D)(ZR_1m)_n(A)TiLpXq$ (I)

$(ZR_1m)_n$ = divalent group bridging D and A;

Z = C, Si, Ge, N, P or B;

R_1 = H or optionally unsaturated 1-20C alkyl, 3-20C cycloalkyl, 6-20C aryl, 7-20C alkylaryl or 7-20 arylalkyl (or two R_1 together form a cycle);

m = 1-2;

n = 1-3;

D = delocalized pi-bonded moiety, which is bound in a eta⁵ bonding mode to Ti;

A = -O-, -S-, -N(R₂)- or -P(R₂)-;

R₂ = H or optionally unsaturated 1-20C alkyl, 3-20C cycloalkyl, 6-20C aryl, 7-20C alkylaryl or 7-20 arylalkyl, optionally containing -OR', -SR', -NR'₂ or PR'₂;

R' = 1-10C alkyl;

L = optionally unsaturated 1-20C alkyl, 3-20C cycloalkyl, 6-20C aryl, 7-20C alkylaryl or 7-20 arylalkyl optionally containing one or more Si or Ge;

X = halo or -OR';

p = 1-2;

q = 0-1;

p + q = 2;

B = alkali or alkaline-earth metal; and

j = 1 (when B is an alkali meta) or 2 (when B is an alkaline-earth metal).

USE - The titanium complexes are used as catalyst components in the polymerization of olefins.

ADVANTAGE - The titanium complexes are obtained in a simple, rapid and economic way. Yields are much higher than in the prior art. The complexes can be readily isolated in high purity by filtration, without the need of laborious purification procedures.

EQUIVALENT-ABSTRACTS:

ORGANIC CHEMISTRY

Preferred Process: The process is carried out in an aprotic solvent.

Preferred Compounds: The titanium complex is preferably a dihydrocarbyl titanium complex of formula (II).

Z = C or Si;

n = 1 or 2;

R₃ = H or optionally unsaturated 1-20C alkyl, 3-20C cycloalkyl, 6-20C aryl, 7-20C alkylaryl or 7-20 arylalkyl, optionally containing Si, Ge, O, S, N or P atoms, or two (or four) adjacent R₃ together form one or more rings;

R₁ = H, methyl, benzyl or phenyl;

R₂ = methyl, ethyl, propyl, butyl, pentyl, hexyl or their isomers, norbornyl, benzyl, phenyl, p-n-butyl-phenyl, cyclohexyl or cyclododecyl; and

L = methyl, neopentyl or benzyl

Preferred Solvent: The aprotic solvent is benzene, toluene, pentane, hexane, heptane, cyclohexane, diethylether and/or tetrahydrofuran.

Preferred Definitions:

(ZR_{1m})_n = CR₁₂, (CR₁₂)₂, C(R₁₂)₃, CR₁=CR₁, SiR₁₂, (SiR₁₂)₂, CR₁₂-SiR₁₂, GeR₁₂, NR₁, PR₁ or BR₁ (preferably Si(CH₃)₂, SiPh₂, CH₂, (CH₂)₂, (CH₂)₃ or C(CH₃)₂);

D = cyclopentadienyl; mono-, di-, tri- or tetra-methyl cyclopentadienyl; 3-tert.-butyl-cyclopentadienyl; 3-adamantyl-cyclopentadienyl; indenyl; 2-methyl-indenyl;

4,7-dimethyl-indenyl; 3-tert.-butyl-indenyl; 3-isopropyl-indenyl; benzoindenyl; 4,5,6,7,-tetrahydroindenyl; fluorenyl; tetrahydrofluorenyl; octahydrofluorenyl; N-methyl- or N-phenyl-5,10-dihydroindeno (1,2-b)indol-10-yl; N-methyl- or N-phenyl-5,6-dihydroindeno(2,1-b)indol-6-yl; azapentalen-6-yl; thiapentalen-6-yl; or mono-, di- or tri-methyl-azapentalen-4-yl;

A = -N(R₂)-, or -P(R₂)-;

R₂ = methyl, ethyl, propyl, butyl, pentyl, hexyl or their isomers, norbornyl, benzyl or phenyl;

p = 2;

q = 0;

L = ethyl, n-butyl, sec-butyl, phenyl, benzyl, -CH₂Si(CH₃)₃ or (preferably) methyl;

X = -OMe, -OEt, -OPr, -OBu, -OBz or (preferably) Cl or Br; and

B = Li or Mg.

Solution of MeLi (11.30 ml) 1.6 M in ether was slowly added at -78degreesC to a solution containing 1.08 g of (tert.-butylamino)(dimethyl)(indenyl)silane, IndSiMe₂NHtBu in 23 ml of ether. The mixture was stirred for 2 hours at room temperature. To the suspension, a mixture of 0.5 ml TiCl₄ in 23 ml n-pentane was added. The mixture quickly turned dark green. At the end of the addition a brown suspension was obtained and stirred overnight. The reaction mixture was evaporated to dryness under reduced pressure. The dark solid was extracted with 60 ml of toluene and then the filtrate was evaporated to dryness under reduced pressure to give 0.99 g (70 % yield) of a gray-black solid. The yield of dimethylsilanediy(tert.-

butylamido)(indenyl)titanium dimethyl obtained with the one-step process according to the invention was much higher than that obtainable with the prior art two reaction step process (lower than 42 %).

TITLE-TERMS: PREPARATION TITANIUM COMPLEX USEFUL
CATALYST COMPONENT POLYMERISE CONTACT
REACT SALT CYCLOPENTADIENYL LIGAND

DERWENT-CLASS: A17 E11 E12

CPI-CODES: A02-A06; A02-A06E1; A02-A07A; A04-G01A; E05-C02; E05-E01; E05-E02; E05-F02; E05-G; E05-L01;

CHEMICAL-CODES: Chemical Indexing M3 *01*
Fragmentation Code A422 A923 A960 B514
B720 B731 B743 B831 G037 G038 G551
M210 M211 M214 M233 M240 M250 M273
M281 M283 M320 M411 M510 M520 M530
M540 M541 M720 N209 N221 N253 N261
N275 N309 N353 N375 N511 N512 Q121
Specific Compounds RA01D3 Registry
Numbers 202032

Chemical Indexing M3 *02*
Fragmentation Code A422 A923 A960 B514
B720 B731 B743 B831 G033 G034 G035
G211 M210 M211 M214 M233 M250 M273
M281 M283 M320 M411 M510 M520 M530
M531 M540 M630 M650 M720 N209 N221
N253 N261 N275 N309 N353 N375 N511
N512 Q121 Specific Compounds RA3C00
Registry Numbers 361277

Chemical Indexing M3 *03*
Fragmentation Code A332 A422 A923 B505
B514 B515 B605 B614 B615 B711 B720
B721 B731 B741 B742 B743 B744 B760
B780 B803 B813 B831 B832 B833 B834
C116 D010 D011 D020 D021 D022 D023

D029 D040 E310 G001 G002 G003 G010
G011 G012 G013 G019 G020 G021 G022
G023 G024 G029 G030 G031 G032 G033
G034 G035 G036 G037 G039 G040 G050
G051 G100 G111 G112 G113 G211 G221
G299 G310 G320 G400 G551 G553 G563
G640 G720 H102 H141 H142 H161 H181
H182 H201 H401 H481 H498 H713 H716
H721 H722 H723 K353 K640 K850 M116
M119 M121 M122 M123 M124 M125 M126
M129 M132 M135 M139 M143 M144 M146
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M322 M323 M331 M332 M333 M340 M342
M343 M344 M351 M361 M373 M391 M392
M393 M411 M510 M511 M520 M530 M531
M532 M533 M540 M541 M542 M543 M720
N209 N221 N253 N261 N275 N309 N353
N375 N511 N512 Q121 Ring Index Numbers
01391 03126 03128 04247 04248 04780
Markush Compounds 003330502

Chemical Indexing M3 *04*
Fragmentation Code A332 A422 A923 A940
A960 A970 B505 B514 B515 B605 B614
B615 B711 B720 B721 B731 B741 B742
B743 B744 B760 B780 B803 B813 B831
B832 B834 C000 C100 C116 C710 C720
D010 D011 D020 D021 D022 D023 D029
D040 E310 G001 G002 G003 G010 G011
G012 G013 G019 G020 G021 G022 G023
G024 G029 G030 G031 G032 G033 G034
G035 G036 G037 G039 G040 G050 G051
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G310 G320 G400 G551 G553 G563 G640
G720 H102 H141 H142 H161 H181 H182
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H716 H721 H722 H723 K353 K640 K850
M116 M119 M121 M122 M123 M124 M125
M126 M129 M132 M135 M139 M143 M144
M146 M147 M149 M150 M210 M211 M212
M213 M214 M215 M216 M220 M221 M222
M223 M224 M225 M226 M231 M232 M233
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M283 M311 M312 M313 M314 M315 M316
M320 M321 M322 M323 M331 M332 M333
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M543 M630 M650 M720 N209 N221 N253
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Q121 Ring Index Numbers 01391 03126
03128 04247 04248 04780 Markush
Compounds 003330501

Chemical Indexing M3 *05*
Fragmentation Code A103 A910 M210 M211
M250 M281 M320 M411 M510 M520 M530
M540 M620 M730 Specific Compounds
R09973 Registry Numbers 130

Chemical Indexing M3 *06*
Fragmentation Code A422 A940 C017 C100
C730 C801 C803 C804 C805 C806 C807
M411 M730 Specific Compounds R05353
Registry Numbers 129667

ENHANCED-POLYMER-INDEXING: Polymer Index [1.1] 018 ;
 G0033*R G0022 D01 D02 D51
 D53; H0000; H0011*R; L9999
 L2573 L2506; L9999 L2528
 L2506; P1150;

Polymer Index [1.2] 018 ;
 ND02;

Polymer Index [1.3] 018 ;
 D01 Ti 4B Tr Si 4A Ge N* 5A
 P* B* 3A D18*R D11 D10
 D13*R F04 F26*R F07*R 7A*R
 D19 D18 D15 D13 D05 D07 D32
 D33 D17 D21 D34 D76 D77 D78
 D79 F86 D56 D59 D68; G3281
 D00 D70 Ti 4B Tr Cl 7A
 R05353 129667; C999 C033
 C000; C999 C340; C999 C157;
 C999 C293; C999 C248;

Polymer Index [1.4] 018 ;
 D01 D15 D13 D75 D68 D11 D10
 D12 D54 D51 D56 D59 D81
 D13*R D18*R 1A*R 2A*R Mg 2A
 7A*R Li 1A Ge 4A Si Cl 7A
 Br; C999 C033 C000; C999
 C157; C999 C340; C999 C248;
 C999 C293;

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: 2001-057214